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REACTIONS OF CYCLOPROPENIUM IONS WITH IMINOPYRIDINIUM YLIDES

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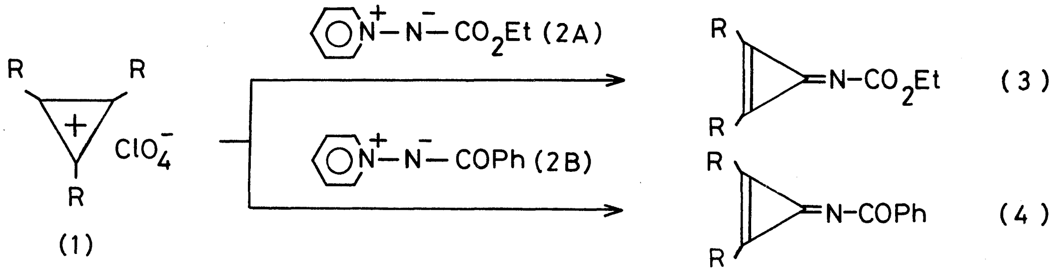
The reaction of heteroatom-substituted cyclopropenium ions (1)[1] with iminopyridinium ylides (2) gave cyclopropenimine derivatives (3 and 4).

Recently, it has been reported that cyclopropenium ions yield thiophenes and thioketones in the reaction of sulfur ylides.[2] However, the reaction of cyclopropenium ions with iminopyridinium ylides are not yet investigated. Thus, the reactions of heteroatom-substituted cyclopropenium ions with N-ethoxycarbonyl- (2A) and N-benzoyl-iminopyridinium ylides (2B) were carried out in various solvents, and cyclopropenimine derivatives (3 and 4) were found to be the reaction products.

Trispyrrolidino- (1a), trispiperidino- (1b), and trishexamethyleneimino-cyclopropenium ions (1c) were employed in the present work. A mixture of the ion (1a-c, 3 mmol) and the ylid (2A and B, 6 mmol) in DMSO (30 ml) was heated at 80°C for 24 hr under nitrogen atmosphere. After standing overnight at room temperature, the solvent was removed under reduced pressure. The resulting residue was washed with ether and then recrystallized from organic solvents to give cyclopropenimine derivatives (3a-c and 4a-c) in 10-35 % yields. Use of other solvent such as chloroform, THF, and HMPA decreased the yields of 3 and 4 except for the case of 4a and 4c. The physical and spectral data of 3 and 4 are shown in Table. Satisfactory elemental analyses and supporting spectral data were obtained for all of 3a-c and 4a-c.



R : 1a, 3a, and 4a = $\underbrace{N(CH_2)_3CH_2}$; 1b, 3b, and 4b = $\underbrace{N(CH_2)_4CH_2}$; 1c, 3c, and 4c = $\underbrace{N(CH_2)_5CH_2}$

Initial nucleophilic attack of ylid nitrogen atom to the carbonium ions (1) followed by elimination of pyridine and substitutent R may lead to the cyclopropenimines (3 and 4).

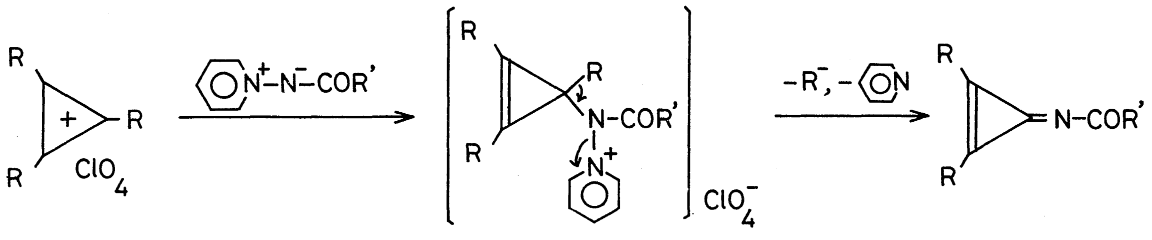


Table. Physical and Spectral Data of 3 and 4

Product	Mp °C	UV* λ nm (log ε)	IR** cm^{-1} ν C=O	 ν C=C	NMR*** δ
3a	126 - 127	238(3.59) 317(2.76)	1630	1540	4.23(q, 2H, J=7.4Hz) 3.57(m, 8H) 1.34(t, 3H, J=7.4Hz) 2.08(m, 8H)
3b	87 - 88	233(3.98) 315(3.68)	1625	1530	4.33(q, 2H, J=7.4Hz) 3.60(m, 8H) 1.38(t, 3H, J=7.4Hz) 1.76(m, 12H)
3c	60 - 62	235(3.59) 315(3.37)	1630	1530	4.10(q, 2H, J=7.4Hz) 3.55(m, 8H) 1.24(t, 3H, J=7.4Hz) 1.68(m, 16H)
4a	108 - 110	234(3.90) 315(3.25)	1590	1540	7.55(m, 5H) 3.53(m, 8H) 2.07(m, 8H)
4b	119 - 120	234(4.02) 317(3.54	1590	1550	7.67(m, 5H) 3.45(m, 8H) 1.70(m, 12H)
4c	89 - 90	234(3.94) 339(3.58)	1590	1550	7.68(m, 5H) 3.63(m, 8H) 1.74(m, 16H)

* Solvent: 3a-c and 4a,b = MeOH; 4c = CH_3CN.

** KBr disk

*** Solvent: 3a,b and 4a,c = $CDCl_3$; 3c = CD_3CN; 4b = CD_3OD.

References

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